

## MEMORANDUM

RE: EFED's Reregistration Chapter C for Naled

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Special Review and Reregistration Division (7508W)

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This memorandum provides a summary of environmental fate and ecological effects, status of data requirements, and recommendations for reducing risk from current use of naled. Attached is the EFED Chapter of the Naled RED.

### **Summary of Environmental Fate and Ecological Effects**

Naled and its degradates are transformed primarily by abiotic hydrolysis, indirect photolysis in water, and biodegradation. Volatilization from soils and/or water is the major mode of transport for naled and its bioactive degradate dichlorvos. Under terrestrial, aquatic, and forestry field conditions naled dissipated rapidly with half-lives of less than 2 days. The dissipation of dichlorvos was also rapid. While naled and dichlorvos are potentially mobile, their degradation is rapid and thus residues of naled, dichlorvos, or naled's other degradates are not likely to leach into ground water. Substantial amounts of naled and its degradates should be available for runoff to surface waters for only one or two days post-application, however, rapid hydrolysis and even faster biodegradation help decrease the concentration of naled and its degradates available for runoff.

No ground or surface water monitoring data for naled or its degradates are available to Environmental Fate and Effects Division at the present time. Therefore, screening models, SCI-GRO for ground water and GENEEC and PRZM/EXAMS for surface water, were used to determine estimated concentrations of naled and dichlorvos in ground and surface water. SCI-GRO model results indicate that the concentrations in

ground water of both compounds are unlikely to exceed 0.01 ppb based upon a maximum annual use rate of 9.375 lb a.i./acre (the use rate on cole crops). Results from the PRZM/EXAMS and GENEEC models also indicate that the impact of both of these chemicals on chronic surface water concentrations will be minimal and approach 0.0 ppb.

Birds and mammals will be exposed to naled through the consumption of bird and mammalian food items containing naled residues and through direct exposure during application. Based on the acute data, application to almonds at 7.2 lbs ai/A on short grass is the only naled use resulting in an avian or mammal risk quotient greater than 0.5. There was no avian chronic toxicity data submitted. There is potential for acute risk to terrestrials mammals when the EEC exceed 460 ppm. Mammals chronic LOC were exceeded for long grass and leaves/leafy crops at all but the lowest rate and on forage at rates of 1.8 lb ai/A and above. Therefore, there is potential for risk to mammals. There is potential for risk to honey bee from the use of naled on blooming crops.

None of the acute EECs exceeded the fish LOC; therefore, risk to freshwater fish is not indicated. Based on 4 and 21-day EECs, there is a potential for chronic risk to freshwater fish from almonds use. The RQ values for shrimp exceeded the LOC of 0.5, acute risk to estuarine/marine invertebrates is expected at rates of 1.9 lb ai/A on citrus. Acute risk to estuarine/marine fish is not expected. The RQ for estuarine/marine invertebrates exceeds the LOC of 1.0, chronic risk is expected for the mosquito control and citrus uses. The aquatic EECs, residue of naled in aquatic environments will not exceed 5-day EC50 for aquatic plants, with the exception of the use on almonds. On almonds, the EECs (32.3 ppb) exceed the 5-day EC50 for *Navicula pelliculosa* (25 ppb). This indicates that hazard to one-cell plants, such as algae and diatoms is unlikely.

### **Status of Data Requirements**

#### **Environmental Fate:**

The naled environmental fate data base is adequate to support reregistration eligibility. Studies on naled's photodegradation in air provide only supplemental information; however, repeat studies are not required at this time.

#### **Water Resources:**

Because no ground or surface water monitoring data for naled or its degradates are available to EFED, screening models were used to estimate environmental concentrations for naled and dichlorvos in ground and surface water.

#### **Ecological Effects:**

The naled ecological toxicology data base is adequate to support registration eligibility; however, additional confirmatory data are needed for the following guidelines:

- 71-4a Avian reproduction (quail),
- 71-4b Avian reproduction (duck),
- 72-4a Early life stage fish (estuarine/marine), and
- 72-4b Life cycle invertebrate (estuarine/marine).

### **Recommendations**

EFED recommends the following items to reduce the ecological risk and to provide a more thorough evaluation of the naled degradates.

1) If HED determines that naled's other degradates are toxicologically significant, we will perform an ecological effects evaluations and estimate the ground and surface water concentrations for these compounds as well.

2) Standard spray drift management labeling should be included on the label.

3) Lengthen the application intervals in days.

4) For aerial application, use a combined 150 feet buffer zone plus 25 feet vegetative buffer zone adjacent to a water body.

## A. Environmental Assessment

### 1. Ecological Toxicity Data

The naled ecological toxicology data base is adequate to support reregistration eligibility, however, additional confirmatory data are needed for the following guidelines:

- 71-4a Avian reproduction (quail)
- 71-4b Avian reproduction (duck)
- 72-4a Early life stage fish (estuarine/marine)
- 72-4b Life cycle invertebrate (estuarine/marine)

#### a. Toxicity to Terrestrial Animals

##### (1) Birds, Acute and Subacute

To establish the toxicity of naled to birds, the following tests are usually required for the technical grade material: one avian single dose oral (LD<sub>50</sub>) study on one species (preferably mallard or bobwhite quail); two subacute dietary studies (LC<sub>50</sub>) on one species of waterfowl (preferably mallard duck) and one species of upland game bird (preferably bobwhite quail).

Avian Acute Toxicity				
Species	% A.I.	LD <sub>50</sub>	MRID	Fulfilled Guideline
Mallard duck	93%	52.2 mg/kg	00160000	Yes
Canada goose	93%	36.9 mg/kg	00160000	Partial*
Sharp-tailed grouse	93%	64.9 mg/kg	00160000	Partial*

\* Partial: when two or more studies are combined to fulfill a data requirement (the Canada goose and Sharp-tailed grouse) .

Based on acute toxicity data, naled is moderately to highly toxic to birds. Avian acute oral studies resulted in LD<sub>50</sub> values of 36.9 to 64.9 mg/kg. The guideline requirement (71-1) for an avian acute oral study has been satisfied. (MRID 00160000)

Avian Subacute Toxicity				
Species	% A.I.	LD <sub>50</sub>	MRID	Guideline
Mallard duck	95%	2724 ppm	00022923	Yes
Bobwhite quail	95%	2117 ppm	00022923	Yes
Ring-necked pheasant	95%	2538 ppm	00022923	Yes
Japanese quail	95%	1327 ppm	00022923	Partial

On a subacute dietary basis, naled is slightly toxic to birds. Four studies produced LC<sub>50</sub> values ranging from 1327 to 2724 ppm. The guideline requirements (71-2a,b) for avian subacute dietary toxicity tests have been satisfied. (MRID 00022923)

## (2) Birds, Chronic

Avian reproduction studies are usually required for an end-use product when birds may be exposed to repeated or continuous exposure to the pesticide. Since naled has uses which involve repeat applications during breeding season, there is potential for repeated exposure to birds. Since avian reproduction studies are not available for naled and data from avian reproduction studies are essential to a complete risk assessment, these data are still required.

## (3) Mammals

The mammalian data available to the Agency indicate that naled is moderately toxic to mammals on an acute basis, with rat LD<sub>50</sub> values ranging from 92 to 371 mg/kg. On a chronic basis, a two-generation reproduction study with rats produced parental and progeny NOELs of 90 ppm (6 mg/kg/day). (MRIDs 00142660 and 00146498)

## (4) Insects

The minimum data required to establish the acute toxicity to honey bees is an acute contact LD<sub>50</sub> on Apis mellifera study with the technical material. One acceptable study was submitted that showed an LD<sub>50</sub> of 0.48 µg ai/bee. This study fulfills the data requirement (141-1) for honey bee acute testing, and shows that naled is highly toxic to honey bees. (MRID 00036935)

When data from the acute study provide an  $LD_{50} < 2 \mu\text{g ai/bee}$ , a foliar residue toxicity study is required. Two acceptable *Apis mellifera* studies were submitted, one was conducted using a 4 lb EC and the other an 8 lb EC formulation. The study using the 4 lb EC formulation applied at 1 lb ai/A, showed that 1-hour residues were highly toxic, while 1-day residues were practically non-toxic to honey bees. The study using the 8 lb EC formulation applied at 0.5 lb ai/A showed that 3-hour residues were low to moderately toxic to the honey bees. These studies fulfill the data requirement (141-2) for honey bee foliar residue testing, and show a significant decrease in residual toxicity from 3 to 24 hours post-treatment. (MRIDs 00060628 and 05000837)

## **b. Toxicity to Aquatic Animals**

### **(1) Freshwater Fish**

To establish the toxicity of a pesticide to freshwater fish, two freshwater fish toxicity studies are minimally required on the technical grade of the active ingredient. One study should use a coldwater species (preferably rainbow trout) and the other a warmwater species (preferably bluegill sunfish).

<b>Acute Studies - Technical on Freshwater Fish</b>				
<b>Species</b>	<b>% A.I.</b>	<b>LC<sub>50</sub></b>	<b>MRID</b>	<b>Fulfilled Guideline</b>
Rainbow trout	90%	195 ppb	40098001	Yes
Rainbow trout	90%	345 ppb	40098001	Yes
Rainbow trout	Tech.	160 ppb	05003107	Yes
Bluegill sunfish	90%	2.2 ppm	40098001	Yes
Cutthroat trout	90%	127 ppb	40098001	Yes
Lake trout	90%	87 ppb	40098001	Yes
Fathead minnow	90%	3.3 ppm	40098001	Yes
Channel catfish	90%	710 ppb	40098001	Yes
Largemouth bass	90%	1.9 ppm	40098001	Yes

These nine 96-hour acute toxicity tests showed that naled is very highly to moderately toxic to freshwater fish, with  $LC_{50}$  values ranging from 87 ppb to 3.3 ppm. The guideline requirements (72-1a and 72-1b) for acute toxicity tests with

the technical pesticide have been satisfied. (MRID No. 40098001, Lake Trout 90%, Fathead Minnow 90% 40098001 and Rainbow Trout Tech. 05003107).

#### Acute Studies - Formulated Product

Formulated product testing on fish may be required when the LC<sub>50</sub> of the technical pesticide is less than the EEC (Estimated Environmental Concentration) in the aquatic environment. The acceptable fish toxicity data on the formulated products are:

<b>Acute Studies - Formulated Product on Freshwater Fish</b>				
<b>Species</b>	<b>% A.I.</b>	<b>LC<sub>50</sub></b>	<b>MRID</b>	<b>Fulfilled Guideline</b>
Rainbow Trout	15%	0.9 ppm	00160740	Yes
Bluegill sunfish	15%	4.0 ppm	00160741	Yes

These studies show that the formulated products of naled are moderately to highly toxic to freshwater fish. The guideline requirements (72-1b and 72-1d) for acute toxicity testing with formulated products have been fulfilled. (MRIDs 00160740 and 00160741)

#### Fish Early Life Stage Test

A fish early life stage test is required when a product is applied directly to water or is expected to be transported to aquatic sites and 1) exposure of aquatic organisms will be continual or recurrent; or 2) the lowest LC<sub>50</sub> is 1 mg/L or less; or 3) the EEC in water is equal to or greater than 0.01 of any LC<sub>50</sub>; or 4) if the EEC is less than any LC<sub>50</sub> and the product has reproductive effects on, or cumulative effects in, aquatic organisms, or has a half-life in water greater than 4 days.

Data on naled fulfill conditions 2) and 3), above. An acceptable early life stage study performed with the fathead minnow and a naled product (94.4% ai) shows that growth is impaired at concentrations greater than 6.9 ppb. The NOEC (growth impaired) is 6.9 ppb, the MATC (Maximum Allowable Toxicant Concentration) based on length and weight is 10 ppb, and the LOEC is 15.0 ppb. The requirement for a fish early life stage study (72-4a) in a freshwater fish has been fulfilled. (MRID 42602201)

## (2) Freshwater Invertebrates

In order to establish the toxicity of a pesticide to freshwater aquatic invertebrates, the minimum data required on the technical grade of the active ingredient is one acute toxicity study. The preferred test species is Daphnia magna.

Acute Studies - Technical on Freshwater Invertebrates				
Species	% A.I.	LC <sub>50</sub>	MRID	Fulfilled Guideline
<u>Daphnia pulex</u>	90%	0.4 ppb	40098001	Yes
<u>Daphnia magna</u>	91.6%	0.3 ppb	00097572	Yes
<u>Simocephalus serrulatus</u>	90%	1.1 ppb	40098001	Yes
Stonefly ( <u>Pteronarycys californica</u> )	90%	8.0 ppb	40098001	Yes
Scud ( <u>Gammarus fasciatus</u> )	90%	18 ppb	40098001	Yes

These studies show that naled is very highly toxic to freshwater aquatic invertebrates ranging from 18 ppb to 0.3 ppb). The guideline requirement for an aquatic invertebrate acute toxicity study (72-2a) has been fulfilled (MRID Nos. 40098001, *Daphnia pulex* and 00097572, *Daphnia magna*).

### Acute Studies - Formulated Product

Formulated product testing on aquatic invertebrates may be required when the EC<sub>50</sub> of the technical pesticide is less than the EEC in the aquatic environment. An acceptable toxicity study on naled formulated product (58% ai) showed an EC<sub>50</sub> of 1.5 ppb, indicating that the formulated product of naled is very highly toxic to freshwater aquatic invertebrates. The guideline requirement (72-2b) for acute toxicity tests with formulated products has been fulfilled. (MRID 00263578)

### Aquatic Invertebrate Life Cycle Study

An aquatic invertebrate life cycle test is required when a product is applied directly to water or is expected to be transported to aquatic sites and 1) exposure of aquatic organisms will be continual or recurrent; or 2) the lowest EC<sub>50</sub> is 1 mg/L



or less; or 3) the EEC in water is equal to or greater than 0.01 of any  $EC_{50}$ ; or 4) if the EEC is less than any  $EC_{50}$  and the product has reproductive effects on, or cumulative effects in, aquatic organisms, or has a half-life in water greater than 4 days.

Data on naled show that it meets the above conditions. Thus, data from a life cycle test were required. A life-cycle study performed with Daphnia magna (97.3% ai) shows that length is affected at concentrations of greater than 0.098 ppb. The NOEC is 0.098 ppb, the MATC is 0.13 ppb, and the LOEC (Lowest Observable Effect Concentration) is 0.18 ppb. The requirement for a freshwater aquatic invertebrate life-cycle study (72-4b) has been fulfilled. (MRID 42908801)

### **(3) Estuarine and Marine Animals**

#### Acute Studies

Acute toxicity testing with estuarine/marine organisms is required when a product is intended for direct application to the estuarine/marine environment or is expected to reach this environment in significant concentrations. The use of naled on agricultural crops and in mosquito control may result in exposure of the estuarine environment.

Estuarine/marine testing requirements include an acute  $LC_{50}$  for an estuarine fish, an acute  $LC_{50}$  for an estuarine shrimp, and either an oyster embryolarvae study or an oyster shell deposition study. The following table summarizes the acceptable submissions:

Acute Studies - Estuarine/Marine Animals				
Species	% A.I.	LC <sub>50</sub>	MRID	Fulfilled Guideline
Sheepshead minnow	90%	1.2 ppm	00160746	Yes
Grass shrimp	90%	92 ppb	40098001	Yes
Grass shrimp	90%	9.3 ppb	00160747	Yes
Eastern oyster	90%	0.19 ppm	00160748	Yes
Eastern oyster	59.6%	170 ppb	42751101	Yes
Sheepshead minnow	59.5%	1.2 ppm	42637201	Yes
Mysid shrimp	59.6%	8.8 ppb	42637202	Yes

These studies characterize naled as very highly toxic to moderately toxic to estuarine fish and invertebrates. The guideline requirements for acute estuarine/marine testing (72-3a, b and c) have been satisfied. (MRID Nos 40098001, 42751101, 42637201, 42637202 and 00160746).

#### Chronic Studies

Estuarine/marine organism chronic tests are required when a product is applied directly to, or is expected to be transported to, estuarine sites and 1) exposure of aquatic organisms will be continual or recurrent; or 2) the lowest EC<sub>50</sub> is 1 mg/L or less; or 3) the EEC in water is equal to or greater than 0.01 of any EC<sub>50</sub>; or 4) if the EEC is less than any EC<sub>50</sub> and the product has reproductive effects on, or cumulative effects in, aquatic organisms, or has a half-life in water greater than 4 days.

Since data on naled show that it meets the above conditions, chronic tests with estuarine/marine organisms are required. Two studies were submitted (sheepshead minnow early life stage MRID No. 429864-01 and mysid life cycle MRID No. 433005-01), however, both studies were invalid. The guideline requirements have not been fulfilled for an estuarine/marine fish early life stage study and an estuarine/marine invertebrate life cycle study using naled.

## c. Toxicity to Plants

### (1) Aquatic

Aquatic plant testing is required for naled as it is registered for aquatic use patterns requiring direct application to wetlands. Data are required on the following species: *Selenastrum capricornutum*, *Lemna gibba*, *Skeletonema costatum*, *Anabaena flos-aquae*, and a freshwater diatom. The acceptable aquatic phytotoxicity data on the technical material are:

Aquatic Plant Toxicity Studies				
Species	% AI	EC <sub>50</sub> (mg ai/L)	MRID	Fulfilled Guideline
<i>Anabaena flos-aquae</i>	94.4	5-day EC <sub>50</sub> = 0.91	42529604	Yes
<i>Skeletonema costatum</i>	94.4	5-day EC <sub>50</sub> = 0.049	42529602	Yes
<i>Navicula pelliculosa</i>	94.4	5-day EC <sub>50</sub> = 0.025	42529603	Yes
<i>Lemna gibba</i>	94.4	NOEC >= 1.8	42529601	Supplemental*
<i>Selenastrum capricornutum</i>	94.4	5-day EC <sub>50</sub> = 0.037	42529605	Supplemental*

\* Although supplemental, study provides sufficient information for use in a risk assessment.

Guideline requirements for aquatic plant testing with naled have been fulfilled. (MRIDs 42529601 through 42529605)

## 2. Environmental Fate Data

The naled environmental fate data base is adequate to support reregistration eligibility. Studies on naled's photodegradation in air provide only supplemental information, however, repeat studies are not required at this time.

### a. Environmental Fate Assessment

Naled and its degradates are transformed largely by chemical hydrolysis and biodegradation. Volatilization from soils and/or water is the major mode of transport for naled and its bioactive degradate dichlorvos. Under terrestrial, aquatic and forestry field conditions naled dissipated rapidly with half-lives of less than 2 days in all three cases. The dissipation of dichlorvos was also rapid. While naled, dichlorvos and the degradate dichloroacetic acid (DCAA) are potentially

mobile, their degradation is rapid and thus residues of naled, dichlorvos or DCAA are not likely to leach into ground water.

Substantial amounts of naled should be available for runoff to surface waters for only one or two days post-application, however, rapid hydrolysis and even faster biodegradation help decrease the concentration of naled available for runoff. Runoff probably occurs by dissolution in runoff water. The degradation products of naled, the bioactive dichlorvos and DCA, also appear to biodegrade readily and to dissipate by volatilization. Thus, dichlorvos or DCA would be available for runoff for a short period of time only. In surface waters, naled and/or its major degradates will not persist long. Naled, dichlorvos and DCA appear to have a low bioaccumulation potential.

Major routes of contamination of surface waters by naled are spray drift and direct application for mosquito abatement. The Agency does not have any monitoring data on the concentrations of naled or its degradates in surface water. It is the Agency's understanding that the registrant intends to satisfy the spray drift requirements by using data generated by the Spray Drift Task Force (SDTF).

The cleavage of the P-O bond in naled and/or dichlorvos can produce other degradates that contain solely the anionic O,O-dimethylphosphate (DMP) group. It has been found that the enzyme organophosphorus hydrolase (OPH) from *Pseudomonas diminuta* MG and *Flavobacterium ATCC27551* is capable of hydrolyzing P-O and P-S bonds (Lai, et al., 1995). The presence of these microorganisms in soil may contribute to the formation of the P-O bond cleavage degradates of naled and/or dichlorvos (DDCA, BDCA and DCA). There are evidences for further possible breakdown of dialkylphosphate anions, such as DMP, by soil bacteria. In the case of DMP, both the methyl groups and the phosphorus are utilized as sources for protein production (Cook, et al., 1978).

## **b. Environmental Fate and Transport**

### **(1) Degradation**

#### Abiotic Hydrolysis

Abiotic hydrolysis studies conducted with  $^{14}\text{C}$ -naled showed that naled degraded rapidly in aqueous media. The rate and mechanism of degradation of naled is pH-dependent, with the rates of degradation increasing with pH. In sterilized buffered solutions maintained at 25°C, the estimated half-lives of hydrolysis were 96 hours (4 days) at pH 5, 15.4 hours (0.64 days) at pH 7, and 1.6 hour (0.07 days) at pH 9. At pH 9, the major degradate was desmethyl naled, but at pH 5 the major degradate was bromodichloro acetaldehyde (BDCA).

Formation of this latter degradate implies cleavage of the P-O bond and elimination of the bromine at the C-2 position. At pH 7 both mechanisms, demethylation and P-O cleavage/C-2 bromine elimination take place. Under the conditions of the abiotic hydrolysis study, there was no evidence of dichlorvos formation at any of the three pH levels studied. (MRIDs 40034902 and 41354101)

#### Photodegradation

Direct photolysis in water does not appear to be a major degradative pathway for naled, however, indirect photolysis in water may be significant. On viable soils the contribution of biodegradation is greater than any contribution from photodegradation. The photodegradation of naled in air is not well defined at this time, but no additional data are required at this time.

#### Photolysis in Water

Direct photolysis is not a major degradative pathway for naled, however, the study conducted in the presence of a chemical photosensitizer (acetone) indicated that indirect photolysis may play an important role in the photodegradation of naled in aqueous media. Moreover, data from the indirect photolysis study indicate that dichlorvos may be produced faster and in higher quantities in the presence of photosensitizers. The rate of degradation for irradiated solutions in the presence of a sensitizer was 0.98 days, in contrast to the approximately 5 days in the absence of the sensitizer. Thus, under environmental conditions naled may photodegrade by indirect photolysis and produce dichlorvos.

In the direct photolysis study, the degradation of naled in a pH 5 buffered solution was controlled by hydrolytic reactions. The half-lives of degradation under irradiated and dark conditions are comparable to the abiotic hydrolysis of naled at pH 5, 25°C. The experimental half-lives ranged from 3.7 days in the abiotic hydrolysis study to 4.7 and 4.4 days in the photodegradation study. The major degradate was BDCA (bromodichloroacetaldehyde), which reached 71-80% by 14 days (end of the study). This degradate is also the major hydrolytic degradate at pH 5 and is formed by cleavage of the P-O bond of naled. Several other degradates were formed in both irradiated and dark solutions, including: desmethyl-naled at maximum 5.4-5.6%; dichlorvos at less than 5%; and desmethyl-DDVP at less than 2% of the applied. Formic acid and glyoxylic acid were exclusively found in irradiated solutions which together reached a maximum of 6.2% combined.

In the indirect photolysis study, dichlorvos reached 20% of the applied levels after 1 day. The other major photolytic degradates, formic acid and

glyoxylic acid, reached a combined maximum of 51.5% of the applied levels after 6 days. Carbon dioxide totaled 22.8% after 6 days, in contrast to only 1.3% after 14 days in the non-sensitized study. The other degradates found were also present in the non-sensitized study, but at lower concentrations.

The photodegradation in water studies were conducted under natural sunlight irradiation. The studies were conducted in Richmond, CA (latitude 37°59'02" N, longitude 122°20'15"W) during the month of August. The daily average intensity was 0.125-0.187 W/cm<sup>2</sup>. (MRIDs 41310702 and 42445103)

#### Photodegradation on Soil

The degradation of naled on sandy loam soil surfaces was rapid, regardless of the presence or lack of natural sunlight exposure. The half-lives of degradation were 0.54 and 0.58 hours under irradiated and non-irradiated conditions. A recalculation of half-life for exposed samples, accounting for degradation rates as total light energy (total cumulative energy) and degradation of naled per J/cm<sup>2</sup>, yielded 0.4 hours. The degradation of naled in or on soils is primarily associated with chemical and microbial processes, with small contribution from photoreactions.

The nature of the degradates was essentially the same for irradiated and dark-control samples. The degradates found were dichlorvos, bromodichloroacetaldehyde (BDCA) and dichloroacetic acid (DCAA). Dichlorvos formed in about equal concentrations under both conditions throughout the duration of the study. While BDCA formed rapidly under both conditions, its concentration decreased after 2 hours. There was a slightly higher concentration of DCAA in exposed samples. Formaldehyde, if formed, appeared to be a transient species. The higher concentration of DCA in exposed samples tends to suggest that photolytical debromination enhances the formation of DCAA from BDCA. The amount of major degradates was BDCA (67-77% between 0.5 -1 hr), DCAA (up to 26% by the end of the study), and dichlorvos at 12% from 0.5 to 2 hr.

This study was conducted with a sandy loam soil (74% sand, 18% silt, 8% clay, 2.2% OM, pH 7.4, cation exchange capacity [CEC] 8 meq/100 g) held at 75% water holding capacity and 25°C. The source of irradiation was natural sunlight at Richmond, CA (latitude 37° 59'02" N and 122° 20'15" W) on August 24, 1989. (MRIDs 41310701 and 42445104)

#### Photodegradation in Air

According to the reported data, naled exposed to natural sunlight degraded with a calculated half-life of 57.8 hours, while naled in dark conditions degraded

with a calculated half-life of 99 hrs. Data suggest that naled degrades quickly under both irradiated and dark conditions. Rather than degrading, naled and its degradates would tend to diffuse into the atmosphere. The material that entered the reaction via evaporation for exposed and dark samples ranged as follows:

	<u>Exposed</u>	<u>Dark</u>
Parent naled	87%(0 hr)-16.6(119hr)	87%(0hr)-28.1(119hr)
Dichlorvos	3%(0 hr)-13%(119 hr)	3%(0 hr)-16%(119hr)
BDCA	4%(0 hr)-55%(119 hr)	4%(0 hr)-43%(119hr)

It is not possible from the experimental set-up used for this study to assess the contribution of wall effects to the photodegradation of naled and dichlorvos. Therefore, the data reported can only be taken as ancillary. (MRIDs 41310703 and 42445102)

### Biodegradation

Although microbial populations in soil and sediment/water systems enhance the degradation of naled and dichlorvos, chemical reactions such as hydrolysis are also involved in the degradation of naled. Under both aerobic and anaerobic conditions naled and its degradates mineralized as the end product of reactions, but CO<sub>2</sub> production is slower under anaerobic than aerobic conditions. Formation of dichlorvos was observed under anaerobic conditions, but dichlorvos was not detected under aerobic conditions due to rapid mineralization. Degradates formed from dichlorvos by cleavage of the P-O, such as DCAA and DCA, were present at higher amounts in the samples incubated under anaerobic rather than aerobic conditions.

### Aerobic Soil Metabolism

Parent naled incubated in Oakley loam sand (85% sand, 6% silt, 9% clay; 1.4% organic matter; pH 7.3; CEC 7.5 meq/g), at a temperature of 25°C and an initial concentration of 10 ppm, degraded rapidly and was practically undetectable after 1 day. In soils under aerobic conditions, mineralization occurred rapidly, with about 50% of the applied radioactivity released as CO<sub>2</sub> after 3 days post-treatment. After 190 days, the total evolved CO<sub>2</sub> was 82%, indicating that the rate of CO<sub>2</sub> release decreased over time. The volatile degradate dichlorvos was not detected under aerobic conditions.

The amount of extractable radioactivity decreased as CO<sub>2</sub> was released. The major degradate extracted from soil was DCAA, reaching about 20% by 2 days post-treatment and declining to less than 1% by 15 days. The degradate

dichloroethanol (DCE) was also detected at about 23% after 1 day and at less than 1% after 15 days. This latter degradate is volatile. Non-extractable degradates increased with time, but reached about 10% after 15 days post-treatment. (MRID 00085408)

#### Anaerobic Aquatic Metabolism

Parent naled incubated at 25°C at a concentration of 8.3 µg/g in sand soil flooded with cranberry bog water degraded with a half-life of less than one day (0.2 to 0.5 day). The soil/water system was kept under nitrogen for 30 days prior to treatment. The amount of naled remaining after 1 day ranged from 12-13% of the applied levels and was not detected after 7 days.

Dichlorvos (at 14-15% of the applied levels) was the major degradate at 1 day post-treatment. The amount of dichlorvos declined to undetectable levels after 62 days. The degradate DCAA reached a maximum concentration of 19-20% after 3 days post-treatment, and declined to 7% 7 days post-treatment. Five unidentified degradates (each less than 7% of the applied) were detected. Unextractable radioactivity from soil ranged from 2.5 to 11% of the applied throughout the duration of the study. Desmethyl-DDVP and 2,2-dichloroethanol (DCE) were identified, each at less than 10% of the applied. Evolution of CO<sub>2</sub> increased with time, reaching 72% at 44 days and approximately 76% after 190 days.

The degradation of dichlorvos, once formed, was slower than that of parent naled. During the first 1-2 days after application of naled, the half-life of dichlorvos was about 0.9 days. After several days, the degradation rate slowed considerably, indicating that the degradation/dissipation of dichlorvos is biphasic. Naled converted rapidly to dichlorvos, but dichlorvos further reacted to other products, with formation and decomposition of dichlorvos probably occurring simultaneously and at comparable rates. The degradation of naled under anaerobic conditions is slower than under aerobic conditions. (MRIDs 40618201, 41354102, 42445101)

## **(2) Mobility**

### Mobility in Soil

The rapid degradation of naled/dichlorvos in soil/water was not conducive to batch-equilibrium studies for these chemicals. Calculation of K<sub>d</sub> values from R<sub>f</sub> values suggests that parent naled and dichlorvos are mobile, however, it appears that dichlorvos is more mobile than naled. Both naled and dichlorvos are less mobile in clay-rich soils.



Soil column leaching studies conducted with naled aged for 0.4 to 3.0 hours showed naled residues were mobile in columns of sand (pH 6.7; 1.9% OM), clay loam (pH 8.1; 2.8% OM), sandy loam (pH 7.1; 1.0% OM) and two loam soils (one of pH 5.5 and 1.5% OM; the other of pH 7.2 and 0.8% OM). The highest mobility of residues was observed in the sand soil column, where 2.7% of the residues remained in the column and 67% was found in the leachates. For the other columns, the radioactive residues remaining in the columns ranged from 5.4 to 11% of the applied while that found in the leachates ranged from 36 to 59%.

In general, the radioactivity remaining was evenly distributed throughout the columns. Parent naled, which was originally applied at 10 ppm, was detected in the leachates at less than 0.02 ppm; dichlorvos at less than 0.093 ppm; DCE at less than 0.085 ppm; DCAA at less than 1.86 ppm and carbonates at less than 0.282 ppm. The latter is an indication of mineralization of naled and degradates, but may not account for any carbon dioxide released as a gas. Loss of dichlorvos or DCE by volatilization was not accounted for.

The degradate DCAA is expected to be very mobile, as suggested by supplemental batch-equilibrium adsorption studies (reported Freundlich adsorption constants of less than 1;  $1/n$  about 1). While this could present a potential ground and/or surface water concern, contamination is not expected as this degradate degrades rapidly in soils under aerobic and anaerobic conditions. (MRIDs 00161100, 40279200, 40394904, 41354104, 41354105 and 41354106)

#### Volatility from Soil--Laboratory

Naled, applied as the 63% EC DIBROM 8 Emulsive at a rate of 2.6 lb ai per acre, volatilized from loamy sand soil at a flux ranging from  $1.19 \times 10^{-4}$  to  $12.5 \times 10^{-4}$   $\mu\text{g}/\text{cm}^2/\text{hour}$ . After 12 days, 48% of the volatilized phase was identified as  $\text{CO}_2$  and 8% as possible dichlorvos (more volatile than parent naled). In soil extracts only about 1% was parent naled, while dichlorvos was approximately 8% and a desmethylated-DDVP (either the mono- or the di-desmethylated degradate or both) comprised about 17% of the applied naled. Several unidentified degradates totaling less than 6% of the applied naled were also found. Non-extractable radioactivity was approximately 9%. Mean air concentration of naled other than  $\text{CO}_2$  ranged from 0.16 to  $1.67 \mu\text{g}/\text{m}^3$ .

Under actual field conditions the volatilization of naled and its volatile degradates will be influenced by the nature of the surface in which naled is present as well as weather conditions such as temperature, humidity and wind speed and direction. (MRIDs 41310704 and 42445105)

### **(3) Accumulation**

#### **Bioaccumulation in Aquatic Organisms**

Static bioaccumulation studies indicated that naled applied at 0.031, 0.063, and 0.127 mg ai/L to tanks inhabited with killifish (*Fundulus heteroclitus*) did not accumulate in whole body tissue over a 7 day exposure period. Dichlorvos was found in fish tissue samples in the 0.063 and 0.127 mg ai/L tanks at 1 hour after exposure at a concentration of 0.04 ppm, but was not detected at later sampling intervals. The dissipation half-life of naled in the tanks was less than 1 day. Dichlorvos was found at 0.02 ppm at 1 day post-treatment, but less than 0.01 ppm was found in all samples taken after 7 days post-treatment. (MRID 00074643; Supplemental)

### **(4) Field Dissipation**

#### **Field Dissipation Studies**

The terrestrial, aquatic and forestry dissipation studies show that naled and dichlorvos dissipate rapidly under environmental conditions, with all three studies indicating a dissipation half-life of less than 2 days. Hydrolysis, biodegradation and possibly reactions with soil surfaces are responsible for the transformation of naled and dichlorvos. Volatilization contributes to the transport of residual naled and dichlorvos. There is no evidence of movement of naled or dichlorvos through the soil profile.

#### **Terrestrial**

A preliminary report submitted to the Agency indicated that parent naled, applied at 2.0 lb ai/A as the 8 lb/gal EC, dissipated with a half-life of less than 2 days on bare plots of sand soil (pH 6.8; CEC 3.30 mg/100g; 4.7% organic matter; 88.8% sand, 8.0% silt, 3.2% clay). Six applications were made during the three week period of the study.

The maximum concentrations of naled were 0.05 - 0.06 ppm 1 day after the last application in the 0 to 5 cm layer. The concentrations of naled were less than 0.01 ppm at the 0 to 10 and 10 to 15 cm depths at any sampling interval. Dichlorvos was detected at 0.02 ppm only at the 0 to 5 cm depth 1 day after the last application. The air temperatures ranged from 51° to 88°F and the cumulative rainfall was 5.1 cm. (MRID 00160040; Supplemental)

### Aquatic

Naled (85% soluble concentrate/liquid), applied at 0.4 lb ai/A/application in five aerial applications over a two week period to ponds in Titusville, FL, and Lexington, MS, dissipated from pond water with a half-life of less than one day. Naled was isolated at a maximum concentration of 0.018 ppm at the Florida site and at 0.006 ppm at the Mississippi site. In general, the concentration of naled decreased with the depth of the water column. Following each application, naled was less than 0.002 ppm after one day post-treatment at the Florida site and less than 0.001 ppm at the Mississippi site. Following the last application, naled was not detected after two days. The degradate dichlorvos was isolated in pond water at maximum concentration of 0.013 and 0.014 at the Florida and Mississippi sites, respectively. Following the last application, dichlorvos was not detected (less than 0.001 ppm) after seven days. Naled and dichlorvos were not detected (less than 0.01 ppm) in the sediments. The sediment at the Florida site was classified as a sand (92-94% sand, 1-3% silt, 5% clay; 1.2- 2.5% OM; pH 7.7; CEC 1.4-2.9 meq/100 g). The sediment at the Mississippi site was classified as silt loam (5% sand, 75% silt, 20% clay; pH 5.2; CEC 11.9 meq/100 g). (MRIDs 40494101, 40976401, 40976402 and 41354107)

### Forestry

Naled, as DIBROM Concentrate 14% EC, applied aerially to 24 acres of loblolly pine in Madison, Georgia at a rate of 0.4 lb ai/acre, dissipated with a half-life of about one day. The highest concentrations of naled and/or dichlorvos, expressed as naled equivalents, were found at the top of the canopy at a maximum of 0.3  $\mu\text{g}/\text{cm}^2$ . In the stream and pond waters the maximum concentrations of naled/dichlorvos were less than 5 ppb (0, 1, 3 days post-treatment). In exposed and litter-covered soil samples, the amount of naled was less than 50 ppb. No naled/dichlorvos residues were found in sediments.

The site contained a stream and a pond, was 600 to 680 feet in elevation, had a 6 to 15% slope, and was underlain with deep (more than 60 inches) sandy loam and sandy clay loam soils of the Madison-Cecil series. (MRIDs 40304301 and 41354108)

## **c. Water Resources**

### **(1) Ground Water**

No ground-water monitoring data for naled or its degradates are available to Environmental Fate and Effects Division (EFED) at the present time. Therefore, the SCI-GROW (Barrett, 1997) screening model was used to estimate “worst case” pesticide concentrations of naled and its degradate, dichlorvos (DDVP) in ground water, for sandy soils with a shallow depth to ground water. Because of the manner in which SCI-GROW was developed, the concentration generated by the model represents an acute and a chronic value. DDVP, which is also a registered pesticide, is the only naled degradate that was examined further in this assessment.

The SCI-GROW model requires three input values-- the aerobic soil metabolism half-life, the soil organic carbon partition coefficient (Koc), and the use rate or the total amount of pesticide applied per year. The aerobic soil metabolism half-lives for naled and DDVP are 1.0 and 0.42 days, respectively. A Koc of 160.0 L/kg, which represents a sandy soil, was selected for naled because naled Koc's for four different soils ranged greater than three-fold (EFED SOP). A Koc of 37.0 L/kg was selected for DDVP; this represents the median Koc of the four different soils (EFED SOP). Naled's annual use rate was calculated by multiplying the application rate by the number of applications during a year for eight different crops (almonds, grapes, cole crops, citrus, safflower, seed alfalfa, cotton, and rangeland for hornfly control). The annual use rate ranged from 9.375 to 2.0 lb a.i./acre.

Naled degrades into DDVP by several processes. As previously mentioned, the maximum amount of DDVP formed from naled is approximately 20 percent of the amount of naled originally applied. Therefore, a conservative DDVP use rate was selected as naled's use rate multiplied by 0.20.

The maximum naled and DDVP SCI-GROW model estimates for ground-water concentrations were for cole crops. The maximum naled and DDVP acute or chronic ground-water concentrations for these cole crops were 0.008 and 0.0002 ppb, respectively. Naled's and DDVP's SCI-GROW ground-water concentrations for almonds, citrus, cole crops, cotton, grapes, safflower, seed alfalfa, and rangeland (for hornfly control) are listed in the following tables.

<b>SCI-GROW Acute and Chronic Ground-Water Concentrations for Naled</b>		
Crop	Acute (ppb)	Chronic (ppb)
Almonds	0.006	0.006
Grapes	0.005	0.005
Cole Crops	0.008	0.008
Citrus	0.005	0.005
Safflower	0.002	0.002
Seed Alfalfa	0.003	0.003
Cotton	0.004	0.004
Rangeland	0.002	0.002

<b>SCI-GROW Acute and Chronic Ground-Water Concentrations for Dichlorvos (DDVP)</b>		
Crop	Acute (ppb)	Chronic (ppb)
Almonds	0.0002	0.0002
Grapes	0.0001	0.0001
Cole Crops	0.0002	0.0002
Citrus	0.0001	0.0001
Safflower	0.0001	0.0001
Seed Alfalfa	0.0001	0.0001
Cotton	0.0001	0.0001
Rangeland	0.00005	0.00005

Even though naled and DDVP are potentially mobile in ground water, they do not persist long enough in ground water to present a contamination concern. Concentrations in ground water of both compounds are unlikely to exceed 0.01 ppb based upon a maximum annual use rate of 9.375 lb a.i./acre (the use rate on cole crops) . Since these concentrations were estimated using the SCI-GROW screening model, which generates “worst case” concentrations , naled will leach to ground water with concentrations at or

below this magnitude.

The geographical location of naled usage for the above seven crops and rangeland indicates a strong preponderance of use in California. The acreages of almonds, grapes, and safflower are 65 percent or more within California. The cole crop acreages are located in several states; however, California has more acreage in these crops than any other state. Alfalfa seeds are primarily grown in the northwestern part of the U.S.; and cotton is grown in Texas (33 percent), California (9 percent), and other southern states near the Mississippi River. Citrus crops are primarily grown in Florida (71 percent) and California (23 percent); and rangeland acreage is restricted to the western states.

## **(2) Surface Water**

EFED does not have any monitoring data on the concentrations of naled or its degradates in surface water; therefore, two different levels or tiers of surface water models were used to estimate conservative surface water concentrations of naled and DDVP. The naled analysis utilized the Pesticide Root Zone Model (PRZM 2.3), that calculates the mass of pesticide leaving the treated field as runoff on a daily basis based upon rainfall events. It calculates both the mass dissolved in runoff and the mass adsorbed to eroding soil. The Exposure Analysis Modeling System (EXAMS 2.94) is a receiving water model. The PRZM model output is used as input to the EXAMS model. Output of the EXAMS model is daily dissolved pesticide concentrations in surface water or the estimated environmental concentrations (EECs). The PRZM and EXAMS models are Tier II models.

GENEEC (GENeric Expected Environmental Concentration program), a Tier I model, was used to estimate conservative surface water concentrations or the EECs for DDVP. A Tier I model is used to screen pesticides to determine which ones potentially pose sufficient risk to warrant higher level modeling.

A detailed description of the naled PRZM and EXAMS modeling is contained in EFED's memorandum entitled *Naled (Dibrom) EECs for Almonds, Citrus, Cole Crops, Cotton, Grapes, Safflower, Seed Alfalfa, Hornflies and Mosquitoes (DP Barcode: D207342)*. This modeling is based upon a high exposure site for pesticide applications on almonds, grapes, cole crops, citrus, safflower, seed alfalfa, cotton, rangeland for hornfly control, and direct applications on ponds for hornflies and mosquitoes control. The weather and agricultural practices were simulated at the sites for 36 years except for almonds (37 years), cotton (26 years), and safflower (22 years) so that the probability of an EEC occurring at those sites could be estimated.

The assumptions for aerial naled applications on the above crops and for direct naled applications on ponds for hornfly and mosquito control are the following:

1. At application, 75 percent of the applied material reaches the 10 Ha

field.

2. Five percent of the applied naled reaches the surface water (1 Ha surface area and 2 m deep pond) at the application time.
3. The remainder of the applied pesticide remains airborne or is deposited on the ground beyond the pond.
4. The aerobic soil metabolism half-life for naled was multiplied by an uncertainty factor of 3, and the result was used as the anaerobic soil metabolism half-life for naled.

The computed naled EECs for the eight crops and two direct pond applications utilizing the PRZM and EXAMS models are listed in the EEC table. The acute and chronic surface water concentrations for naled are the maximum initial EEC and 90 day EEC, respectively, for each crop. The overall maximum acute and chronic surface water concentrations for naled are for almonds. However, since almonds are grown in arid environments, it is unlikely that pesticides applications here will affect drinking water sources. Therefore, the acute and chronic values generated for citrus (23.7 and 1.0 ppb, respectively) were used instead. Tables listing the pertinent input parameters and modeling results for the citrus PRZM/EXAMS run are provided as examples of these items. However, because of naled's rapid abiotic hydrolysis rate (0.64 days), its impact on chronic surface water concentrations should approach 0.0 ppb.

### The Estimated Environmental Concentrations (EECs) for Naled

[ Results reported are 1 in 10 year maximum values with 5% spray drift. The asterisk (\*) indicates proposed label changes which are not on the current label.]

Crop	Application Method	Applica. Rate lb a.i./acre (Number of Applications)	Max Initial EEC (PPB)	4 DAY EEC (PPB)	21 DAY EEC (PPB)	60 DAY EEC (PPB)	90 DAY EEC (PPB)
Almonds	Airblast	7.20 (1)	32.3	11.0	2.6	1.45	0.97
Grapes	Airblast	0.938 (6)	5.9	1.5	0.51	0.48	0.32
Cole crops	Aerial	1.875* (5)	12.7	3.1	1.1	0.84	0.56
Citrus	Airblast	1.875* (3)	11.1	2.4	0.85	0.50	0.34
Citrus	Airblast	1.875 (7)	23.7	6.5	1.7	1.5	1.0
Safflower	Aerial	0.70 (3)	1.9	0.43	0.25	0.14	0.09
Safflower	Aerial	0.70 (6)	2.0	0.49	0.28	0.26	0.19
Seed Alfalfa	Aerial	1.40 (3)	3.9	0.86	0.50	0.27	0.18
Cotton	Aerial	0.938 (5)	7.0	1.9	0.61	0.48	0.32
Mosquitoes:							
Direct Application	Pond	0.1 (3) 0.25 (3)	0.379 0.948	0.179 0.448	0.035 0.088	---	---
Hornflies:							
Rangeland	Aerial	0.40 (5)	3.5	0.92	0.29	0.22	0.15
Direct Application	Pond (Aerial)	0.40 (5)	1.12	0.25	0.14	--	--



NALED CHEMICAL CHARACTERISTICS, LOCATION  
AND MANAGEMENT PRACTICES FOR **CITRUS**

Modeler:	Siroos Mostaghimi
Runoff Model:	PRZM2
Receiving Water Model:	EXAMS 2.94
<b><u>CHEMICAL</u></b> <b>Common Name:</b> <b>Formulation:</b> <b>Parameters:</b> Hydrolysis $T_{1/2}$ : pHs 5, 7 and 9 Aerobic Soil $T_{1/2}$ : Anaerobic soil $T_{1/2}$ : Aerobic Aquatic $T_{1/2}$ : Anaerobic Aquatic $T_{1/2}$ : Solubility: Vapor Pressure: $K_{oc}$ :	Naled (Dibrom) Soluble Concentrate  96, 15.4 and 1.6 Hours 1 day 3 days (estimated) 1.5 days 4.5 days 2000 mg/L 4.5 E-4 Torr 180 L/Kg
<b><u>LOCATION:</u></b> Crop: MLRA: Soil Series: Texture: County: State: Justification:	Citrus U-154 Adamasville Sand Lake Florida Reasonable high exposure
<b><u>MANAGEMENT:</u></b> Tillage Type: Application Method: Percent Spray drift: Planting Date: Emergence Date: Maturity Date: Harvest Date:	Conventional Airblast 5% 1/10 5/11 7/17 8/1

PRZM/EXAMS MODELING RESULTS FOR APPLICATION OF NALED  
ON CITRUS

<b><u>PESTICIDE APPLICATION:</u></b>	
Application Rate:	1.875 lb ai/Acre
Application date(s):	5/20, 5/27, 6/3
Justification:	Rate Proposed by registrant
<b><u>RESULTS:</u></b>	
<b>10 Year Return (10% Exceedence)</b>	
Max Initial:	11.1 µg/L
96 Hour (acute):	2.4 µg/L
21 Day (chronic):	0.85 µg/L
60 Day max:	0.50 µg/L
90 day max:	0.34 µg/L
Average Yearly Rainfall:	140.6 cm
Average Yearly Runoff:	9.16 cm
Average Erosion Rate:	0.20 Mg/Ha
<b><u>LOADING BREAKDOWN:</u></b>	
Runoff:	28.0 %
Erosion:	0.0 %
Spray Drift:	72.0 %

GENEEC (Parker *et al*, 1995) is a screening model designed by EFED to estimate the concentrations found in surface water for use in ecological risk assessment. As such, it provides upper-bound values on the concentrations that might be found in ecologically sensitive environments because of the use of a pesticide. It was designed to be simple to use and to only require data which is typically available early in the pesticide registration process. GENEEC is a single event model (one runoff event), but can account for spray drift from multiple applications. GENEEC represents a 10 hectare field immediately adjacent to a 1 hectare pond that is 2 meters deep with no outlet. The pond receives a spray drift event from each application plus one runoff event. The runoff event moves a maximum of 10 percent of the applied pesticide into the pond. This amount can be

reduced due to degradation on the field and the effects of soil sorption. Spray drift is estimated at 5 percent of the application rate.

The input values for the GENEEC model runs for DDVP are the aerobic soil metabolism half-life, the aerobic aquatic metabolism half-life, the hydrolysis (pH 7) half-life, the photolysis half-life, the water solubility, the Koc, and an estimated DDVP application rate (0.20 of the original naled application) for each crop. The Koc value was based upon the average soil partition coefficient ( $K_d$ ) and organic carbon content for four different soils evaluated during the naled study (EFED SOP). The input values for the DDVP GENEEC model runs are listed in the following table.

<b>GENEEC Input Parameters for Dichlorvos (DDVP)</b>	
<b>Chemical</b>	Dichlorvos (DDVP)
<b>PC Code</b>	84001
<b>Solubility</b>	15,600 mg L <sup>-1</sup>
<b>Hydrolysis Half-life (days) @ pH 7</b>	5.19
<b>Photolysis Half-life (days)</b>	0.625
<b>Aerobic Soil Metabolism (days)</b>	0.42
<b>Aerobic Aquatic Metabolism (days)</b>	no data *
<b>Soil Organic Carbon Partition Coefficient</b>	89 L/kg
<b>Source and Quality</b>	EFED Naled RED chapter and preliminary fate assessment for DDVP
<b>Prepared By</b>	J. Peckenpaugh
<b>Date</b>	October 6, 1997
<b>Crops</b>	almonds, grapes, cole crops, citrus, safflower, seed alfalfa, cotton, and rangeland
<b>Application Rate (lb a.i./acre)</b>	variable from .080 to 1.44 ( 0.20 of naled application rate)
<b>Number of Applications</b>	variable from 1 to 6
<b>Application Method</b>	aerial

\* Approximated as 0 days half-life.

The results of the GENEEC model runs for DDVP are listed in following table. The peak and 56 day EEC concentrations in this table represent the acute and chronic surface water concentrations, respectively, for DDVP. The maximum DDVP estimates

for surface water concentrations were obtained for naled applications on almonds. However, the acute and chronic surface water concentrations for cole crops (16.5 and 2.2 ppb, respectively) were used as the maximum overall values because pesticide applications on almonds, which are grown in an arid environment, are not a significant potential drinking water contaminant.

GENEEC EECs for Dichlorvos (DDVP)				
Crop	Peak (ppb)	4 Days (ppb)	21 Days (ppb)	56 Days (ppb)
Almonds	61.4	50.4	20.9	8.2
Grapes	8.3	6.8	2.8	1.1
Cole Crops	16.5	13.6	5.6	2.2
Citrus	16.4	13.5	5.6	2.2
Safflower	6.1	5.1	2.1	0.8
Seed Alfalfa	12.3	10.1	4.2	1.7
Cotton	8.3	6.8	2.8	1.1
Rangeland	3.5	2.9	1.2	0.5

Substantial amounts of naled and DDVP are potentially available for runoff to surface waters for **only** a few days post-application. Even though both these chemicals are mobile, they have a low persistence. If a runoff event occurs very soon (1-2 days) after an application and if naled or DDVP is transported into surface water, naled will degrade rapidly (half-life < 1 day) and DDVP will persist slightly longer (half-life ~ 5 days). Therefore, the impact of both of these chemicals on chronic surface water concentrations will be minimal and approach 0.0 ppb.

### **3. Exposure and Risk Characterization**

#### **a. Ecological Exposure and Risk Characterization**

##### **(1) Non-target Terrestrial Animals**

Birds and mammals will be exposed to naled through the consumption of insect and plant food material containing naled residues and through direct exposure during application. To assess acute hazard to terrestrial organisms, the following formulas are used:

$$\text{Risk Quotient (RQ)} = \text{EEC}/\text{LC}_{50}$$

$$\text{Level of Concern (LOC)} = 0.5$$

When the RQ exceeds the LOC, acute risk is possible.

Although actual residue data were submitted for naled; sampling for these data was not conducted immediately following application or even on the day of application. Therefore, these data cannot be used in support of the chronic assessment for mammals.

### (a) Birds

#### Risk Presumption For Terrestrial Animals

<u>Risk Presumption</u>	<u>RQ</u>	<u>LOC</u>
Birds		
Acute High Risk	EEC/LC50 or LD50/sift or LD50/day	0.5
Acute Restricted Use	EEC/LC50 or LD/sift or LD50/day (or LD50 < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC50 or LD50/sift or LD50/day	0.1
Chronic Risk	EEC/NOEC	1.0
Wild Mammals		
Acute High Risk	EEC/LC50 or LD/sift or LD50/day	0.5
Acute Restricted Use	EEC/LC50 or LD50/sift or LD50/day (or LD50 < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC50 or LD50/sift or LD50/day	0.1
Chronic Risk	EEC/NOEC	1.0

#### Acute Effects

For birds, the LC<sub>50</sub> value for the most sensitive species is 2117 ppm. The

following table provides the terrestrial EECs and the acute risk quotients for birds.

<b>Residues (ppm) and Risk Quotients (RQ) for Avian Species and Mammals</b>								
<b>Appl. Rate lb ai/A</b>	<b>Short Grass Residue</b>	<b>Short Grass RQ</b>	<b>Long Grass Residue</b>	<b>Long Grass RQ</b>	<b>Leafy Residue</b>	<b>Leafy Crop RQ</b>	<b>Alfalfa, Clover Residue</b>	<b>Alfalfa, Clover RQ</b>
0.7 (safflower)	166	0.08	78	0.04	88	0.04	41	0.02
0.9 (grapes)	229	0.11	104	0.05	120	0.06	54	0.03
1.4 (seed alfalfa)	333	0.16	156	0.07	177	0.08	83	0.04
1.9 (citrus/cole)	458	0.22	208	0.10	234	0.11	109	0.05
7.2 (almonds)	1700	0.80	790	0.37	900	0.43	420	0.20

The application to almonds at 7.2 lb ai/acre on short grass is the only naled use resulting in a risk quotient greater than 0.5. At this rate, the EEC is 1700 ppm and the RQ is 0.8, indicating potential high risk to birds.

#### Chronic Effects

Avian reproduction studies are not available for naled. Although the half-life of naled, 1-2 days in the field, indicates that naled will not persist in the environment; the labels provide no restrictions on the number or intervals of application. In addition, some of the use sites are high exposure sites for birds. Therefore, there is still a significant potential for continuous or repeated exposure to birds and a potential for chronic avian risk.

In the absence of avian reproduction data, the Agency cannot conduct an assessment for chronic risk to birds. These studies will provide the Agency with the information necessary to assess this potential risk and this data requirement is still outstanding.

## **(b) Mammals**

### Acute Effects

Data show naled to be moderately toxic to mammals on an acute basis (rat  $LD_{50} = 92$  to  $371$  mg/kg). In the absence of mammalian  $LC_{50}$  data, the risk assessment was based on the  $LD_{50}$  value, as follows:

Average food consumption for a young rat is 10 g per day. If toxicant is present in/on the food item at 920 ppm, 10 g of food will contain 9.2 mg of toxicant. Since the representative weight of a young rat is 0.1 kg, daily intake is 9.2 mg toxicant/0.1 kg body weight or 92 mg toxicant/kg body weight. This daily intake equals the actual  $LD_{50}$  value of 92 mg/kg. For this calculation,  $RQ = EEC/920$  ppm, and an acute risk is indicated when the risk quotient is greater than 0.5. Thus, there is potential for acute risk to mammals when terrestrial EECs exceed 460 ppm.

As can be seen in the residue table above, residues are expected to occur at this level only after application to almonds at 7.2 lb ai/acre.

### Chronic Effects

Although environmental fate data indicate that naled will not persist in the environment, many naled uses involve multiple applications at short intervals. Therefore, there is still a significant potential for continuous or repeated exposure to mammals and the potential for chronic risk to mammals.

The Agency conducted an assessment using data from a rat reproduction study that indicated a rat reproduction (progeny) NOEL of 6 mg/kg/day or 90-120 ppm in the diet. For assessment of chronic risk to mammals, the risk quotient is equal to the  $EEC/NOEL$  and the Level of Concern (LOC) is 1.0. Based on these values, whenever the EEC exceeds the NOEL, there is potential chronic risk. The use of naled at current rates presents a potential for chronic risk to mammals. The following table outlines the expected residue levels at various application rates, and provides the chronic risk quotients for mammals. EECs were generated using the Kenaga nomograph.

<b>Residues (ppm) and Risk Quotients (RQ) for Avian Species and Mammals</b>								
<b>Appl. Rate lb ai/A</b>	<b>Short Grass Residue</b>	<b>Short Grass RQ</b>	<b>Long Grass Residue</b>	<b>Long Grass RQ</b>	<b>Leafy Residue</b>	<b>Leafy Crop RQ</b>	<b>Alfalfa, Clover Residue</b>	<b>Alfalfa, Clover RQ</b>
0.7 (safflower)	166	1.8	78	0.9	88	1.0	41	0.5
0.9 (grapes)	229	2.5	104	1.2	120	1.3	54	0.6
1.4 (seed alfalfa)	333	3.7	156	1.7	177	2.0	83	0.9
1.9 (citrus/cole)	458	5.1	208	2.3	234	2.6	109	1.2
7.2 (almonds)	1700	18.9	790	8.8	900	10.0	420	4.7

As shown in the table, residues on short grass exceed the mammalian chronic LOC at all application rates. The LOC is exceeded on long grass and leaves/leafy crops at all but the lowest rate and on forage at rates of 1.8 lb/A and above. These values indicate significant potential for chronic risk to mammals. The potential for chronic risk is especially significant because naled may be applied frequently at short intervals and because some of the registered use sites (citrus, grapes, seed alfalfa) are high exposure sites for mammals.

In view of the above, the Agency concludes that the use of naled at current rates presents significant potential for chronic risk to mammals.

#### **© Insects**

Data from an acute study showed naled to be highly toxic to honey bees. Data from foliar residue studies showed a significant decrease in residual toxicity from 3 to 24 hours post-treatment. Acute risk to bees is anticipated from the use of naled on blooming crops. The extent of the residual hazard will vary with application rate, weather conditions and the formulation of the specific product applied.

#### **(2) Exposure and Risk to Non-target Aquatic Animals**



### (a) Freshwater Fish and Invertebrates

Fish and aquatic invertebrates will be exposed to naled through drift and runoff from treated areas and through direct exposure of wetlands and aquatic habitats from mosquito control applications.

#### Acute Effects

##### Risk Presumption For Aquatic Animals

<u>Risk Presumption</u>	<u>RQ</u>	<u>LOC</u>
Acute High Risk	EEC/LC50 or EC50	0.5
Acute Restricted Use	EEC/LC50 or EC50	0.2
Acute Endangered Species	EEC/LC50 or EC50	0.05
Chronic Risk	EEC/MATC or NOEC	1.0

For the aquatic acute risk assessment, the RQ is defined as  $EEC/LC_{50}$ , where the LOC is 0.5. Ecotoxicity values used in this assessment are the lake trout  $LC_{50}$  (87 ppb) and the *Daphnia magna*  $EC_{50}$  (0.3 ppb). EEC values and RQ provided in the following tables are based upon these assumptions:

1. 95% of the applied chemical reaches the field during application
2. 1% of applied naled reaches surface water during application
3. 4% remains airborne or is deposited on the ground beyond the pond
4. An anaerobic half life metabolism was estimated by multiplying the aerobic soil metabolism half life by 3 (uncertainty factor)

The EECs for hornflies and mosquitoes are reported as a direct application of naled to the pond.

The following tables show the naled use rates, EECs and RQ for each crop. The 1 in 10 year maximum instantaneous, 96-hour acute, and 21-day chronic average dissolved naled concentrations with 1% spray drift are reported in these tables.

Estimated Residues (ppb) and Risk Quotients (RQ) for Freshwater Organisms				
Crop	Appl. Rate lb ai/A (# appls.)	Inst. EEC (ppb)	Fish Risk Quotient	Invert. Risk Quotient
Safflower	0.7 (6)	2.0	0.02	6.67
Seed Alfalfa	1.4 (3)	3.9	0.05	13.00
Mosquitoes (Direct)	0.1 (3)	0.4	0.004	1.26
	0.25 (5)	0.9	0.01	3.16
Hornflies (Direct)	0.4 (5)	3.5	0.04	11.67
	0.1 (5)	1.1	0.01	3.73
Grapes	0.9 (6)	5.9	0.07	19.67
Cole Crops	1.9 (5)	12.7	0.15	42.33
Cotton	0.94 (5)	7.0	0.08	23.33
Almonds	7.2 (1)	32.3	0.37	107.67
Citrus	1.9 (3)	11.1	0.13	37.00
	1.9 (7)	23.7	0.27	79.00

The freshwater fish LOC will be exceeded for any EEC greater than 43.5 ppb and the aquatic invertebrate LOC will be exceeded for any EEC greater than 0.15 ppb. None of the EECs exceed the fish LOC; therefore, risk to freshwater fish is not indicated. Since EECs for all major uses greatly exceed the aquatic invertebrate LOC, acute risk to freshwater aquatic invertebrates can be expected with all major uses of naled.

#### Chronic Effects

For the aquatic chronic risk assessment, the risk quotient is equal to the EEC/MATC, and the LOC is 1.0. The risk assessment used ecotoxicity values from the maximum acceptable toxicant concentrations (MATCs) for fathead minnow (10.0 ppb) and *Daphnia magna* (0.13 ppb). Using these values, the chronic fish LOC is exceeded for any EEC greater than 10.0 ppb and the chronic aquatic invertebrate LOC is exceeded for any EEC greater than 0.13 ppb:

Estimated Residues (ppb): Chronic Exposure							
Crop	Appl. Rate lb ai/A (# appls.)	4-Day EEC (ppb)	4-Day Fish RQ	4-Day Invert. RQ	21-Day EEC (ppb)	21-Day Fish RQ	21-Day Invert. RQ
Safflower	0.7 (6)	0.5	0.05	3.77	0.3	0.03	2.15
Seed Alfalfa	1.4 (3)	0.9	0.09	6.62	0.5	0.05	3.85
Mosquitoes (Direct)	0.1 (3) 0.25 (3)	0.2 0.5	0.02 0.05	1.38 3.45	0.0 0.1	0.00 0.01	0.27 0.68
Hornflies (Rangeland) (Direct)	0.4 (5) 0.4 (5)	0.9 0.3	0.09 0.03	7.08 1.92	0.3 0.1	0.03 0.01	2.23 1.08
Grapes	0.9 (6)	1.5	0.15	11.54	0.5	0.05	3.92
Cole Crops	1.9 (5)	3.1	0.31	23.85	1.1	0.11	8.46
Cotton	0.9 (5)	1.9	0.19	14.62	0.6	0.06	4.69
Almonds	7.2 (1)	11.0	1.10	84.62	2.6	0.26	20.00
Citrus	1.9 (3)	2.4	0.24	18.46	0.9	0.09	6.54
	1.9 (7)	6.5	0.65	50.00	1.7	0.17	13.08

Based on 4-day and 21-day EECs, there is a potential for chronic risk to freshwater fish from use almonds. There is significant potential for chronic risk to freshwater invertebrates from all major naled uses.

### (b) Estuarine and Marine Animals

#### Acute Effects

Since EECs based on modeling are not yet available for estuarine and marine environments, freshwater EECs were used to estimate exposure in these environments. Citrus and mosquito control are major uses of naled that generate estuarine concerns. Maximum freshwater EECs are 11.1 ppb and 23.7 ppb (citrus; 3 and 7 applications, respectively) and 0.379 and 0.948 ppb (mosquito control; 0.1 and 0.25 lb a.i./A, respectively). Acute LC<sub>50</sub> values for estuarine organisms are:

Sheepshead minnow LC<sub>50</sub> = 1.2 ppm;  
Mysid shrimp LC<sub>50</sub> = 8.8 ppb;  
Oyster shell deposition EC<sub>50</sub> = 170 ppb.

Using these data, RQ values for citrus are 0.01 (11.1/1200) and 0.02

(23.7/1200) for sheepshead minnow, 1.26 (11.1/8.8) and 2.69 (23.7/8.8) for mysid shrimp and 0.07 (11.1/170) and 0.14 (23.7/170) for oyster. Since RQ values for shrimp exceed the LOC of 0.5, acute risk to estuarine/marine invertebrates is expected at rates of 1.9 lb a.i./A on citrus. Acute risk to estuarine/marine fish is not expected from use on citrus.

For mosquito control, with an EEC of 0.948 ppb, RQ are 0.00 (0.948/1200) for sheepshead minnow, 0.11 (0.948/8.8) for mysid shrimp and 0.01 (0.948/170) for oyster. None of the RQ exceed the LOC of 0.5. Thus, risk to estuarine/marine invertebrates is not expected from the mosquito control use.

### Chronic Effects

Since EECs based on modeling are not yet available for estuarine and marine environments, freshwater EECs were again used to estimate exposure in these environments. Citrus and mosquito control are the two major uses of naled that generate estuarine concerns. Maximum chronic EECs are 2.4 and 6.5 ppb for citrus (3 and 7 applications, respectively) and 0.179 and 0.448 ppb for mosquito control (0.1 and 0.25 lb a.i./A, respectively). Since no estuarine chronic ecotoxicity data are available, calculations were based on the freshwater toxicology data used above.

Using these data, RQ for citrus are 0.24 (2.4/10) and 0.65 (6.5/10) for fish and 18.46 (2.4/0.13) and 50.00 (6.5/0.13) for invertebrates. Since the RQ for invertebrates exceed the LOC of 1.0, chronic risk to estuarine/marine aquatic invertebrates is expected from use on citrus.

For mosquito control, chronic RQ are 0.02 (0.179/10) and 0.05 (0.448/10) for fish and 1.38 (0.179/0.13) and 3.45 (0.448/0.13) for aquatic invertebrates. Since the RQ for aquatic invertebrates exceed the LOC of 1.0, chronic risk to estuarine/marine invertebrates is expected from the mosquito control use.

Ecotoxicology data for chronic effects in estuarine/marine animals, specifically an estuarine fish early life stage and a shrimp life cycle test, are required to greatly reduce the uncertainty in this assessment.

## **(2) Exposure and Risk to Plants**

### **(a) Aquatic**

Aquatic plants will be exposed to naled through drift and runoff from treated areas, and through direct exposure of wetlands and aquatic habitats from mosquito control applications.

Based on aquatic plant toxicity data and calculated aquatic EECs, residues of naled in aquatic environments will not exceed 5-day EC<sub>50</sub>s for aquatic plants, with the exception of the use on almonds. On almonds, the EEC (32.3 ppb) exceeds the 5-day EC<sub>50</sub> for *Navicula pelliculosa* (25 ppb). This indicates that hazard to one-celled plants, such as algae and diatoms is unlikely.

Residues of naled will not exceed the NOEC for *Lemna gibba*. Hazard to vascular plants is expected to be minimal.

### (b) Endangered Species

#### Terrestrial

Risk assessments for endangered birds and mammals are identical to those for non-endangered birds and mammals, except that the acute LOCs for endangered species are more conservative (0.1 vs. 0.5). Chronic LOCs remain unchanged.

For birds, the LC<sub>50</sub> value for the most sensitive species is 2117 ppm. The following table provides the terrestrial EECs and the acute risk quotients for birds. The same table was used in the assessment of acute effects for non-endangered birds.

Residues (ppm) and Risk Quotients (RQ) for Avian Species								
Appl. Rate (lb ai/A)	Short Grass Residue	Short Grass RQ	Long Grass Residue	Long Grass RQ	Leafy Residue	Leafy Crop RQ	Alfalfa, Clover Residue	Alfalfa, Clover RQ
0.7 (safflower)	166	0.08	78	0.04	88	0.04	41	0.02
0.9 (grapes)	229	0.11	104	0.05	120	0.06	54	0.03
1.4 (seed alfalfa)	333	0.16	156	0.07	177	0.08	83	0.04
1.9 (citrus/cole)	458	0.22	208	0.10	234	0.11	109	0.05
7.2 (almonds)	1700	0.80	790	0.37	900	0.43	420	0.20

As shown in the above table, application to grapes, seed alfalfa, citrus, cole crops, and almonds may result in residues on short grass that exceed the acute LOC for birds. The LOC is also exceeded on leaves/leafy crops from application

to citrus, cole crops and almonds, as well as long grass and forage from application to almonds. On the basis of this information, there is a potential for acute risk to endangered birds.

In the absence of mammalian  $LC_{50}$  data, risk to nonendangered mammals was assessed using values extrapolated from the rat  $LD_{50}$ . For this endangered species calculation, RQ was calculated as  $EEC/920$  ppm with acute risk indicated by a risk quotient greater than 0.1. Thus, acute risk to endangered mammals is expected when the terrestrial EEC exceeds 92 ppm.

As can be seen from the above table, residues greater than 92 ppm will be found on short grass for all applications, on long grass and leaves/leafy crops for all but the safflower use, and on forage for the citrus, cole crop, and almond uses. Thus, there is a potential for acute risk to endangered mammals.

The risk assessment for non-endangered mammals indicated a potential for chronic risk; the same conclusion applies for endangered species of mammals. Since avian reproduction data are lacking, an assessment of chronic risk to endangered birds cannot be made at this time.

#### Aquatic

The assessments for endangered and non-endangered aquatic organisms are identical, except that the acute LOC for endangered species is more conservative (0.05 vs. 0.5). The chronic LOC remains unchanged. EECs and acute risk quotients are as follows:

Estimated Residues (ppb) and Risk Quotients (RQ) for Freshwater Organisms				
Crop	Appl. Rate lb ai/A (# apps.)	Inst. EEC (ppb)	Fish Risk Quotient	Invert. Risk Quotient
Safflower	0.7 (6)	2.0	0.02	6.67
Seed Alfalfa	1.4 (3)	3.9	0.05	13.00
Mosquitoes (Direct)	0.1 (3)	0.4	0.00	1.26
	0.25 (5)	0.9	0.01	3.16
Hornflies (Rangeland) (Direct)	0.4 (5)	3.5	0.04	11.67
	0.4 (5)	1.1	0.01	3.73
Grapes	0.9 (6)	5.9	0.07	19.67
Cole Crops	1.9 (5)	12.8	0.15	42.33
Cotton	0.9 (5)	7.0	0.08	23.33
Almonds	7.2 (1)	32.3	0.37	107.67
Citrus	1.9 (3)	11.1	0.13	37.00
	1.9 (7)	23.7	0.27	79.00

As indicated, the RQ for endangered fish exceed the LOCs for the use of naled on grapes, cole crops, cotton, almonds and citrus. The RQ for aquatic invertebrates exceed the LOCs for all uses.

The Agency has concluded that the use of naled on almonds at current rates presents significant potential for chronic risk to fish. Thus, endangered fish species associated with naled use on almonds may be at risk. The Agency has concluded that all major uses of naled present significant potential for chronic risk to aquatic invertebrates. Thus, endangered species of aquatic invertebrates may be at risk.

#### Plants

There is no evidence for risk to endangered plants from use of naled.

## Endangered Species Protection Program

The Endangered Species Protection Program is expected to become final in the future. Limitations on the use of naled may be required to protect endangered and threatened species, but these limitations have not been defined and may be formulation specific. EPA anticipates that a consultation with the Fish and Wildlife Service may be conducted in accordance with the species-based priority approach described in the Program. After completion of this consultation, registrants will be informed if any required label modifications are necessary. Such modifications would most likely consist of the generic label statement referring pesticide users to use limitation contained in county bulletins.

### **b. Water Resources Risk Implication for Human Health**

#### **(1) Ground Water**

Naled, DDVP, and naled's other degradates are not regulated under the Safe Drinking Water Act. Thus, neither MCLs nor drinking water health advisories have been established for these compounds. The SCI-GROW screening model's evaluation of naled and DDVP indicates that neither compound will persist in ground water. Concentrations in ground water of both compounds, applied at the maximum label rates for eight different crops, are unlikely to exceed 0.01 ppb for either the acute or chronic values (p17).

#### **(2) Surface Water**

No monitoring data on the concentrations of naled or DDVP was available to EFED. Therefore, PRZM and EXAMS modeling were used to estimate naled concentrations in surface water; and the GENEEC model was used to estimate conservative surface water concentrations for DDVP. Naled's acute and chronic PRZM\EXAMS values were 23.7 and 1.0 ppb, respectively, for citrus. However, because of naled's rapid abiotic hydrolysis rate (0.64 days), the chronic surface water values should approach 1.0 ppb. DDVP's acute and chronic GENEEC values were 16.5 and 2.2 ppb, respectively, for cole crops.

Substantial amounts of naled and DDPV are potentially available for runoff to surface waters for **only** a few days post-application. Even though both these chemicals are mobile, they have a low persistence. If a runoff event occurs very soon (1-2 days) after an application and if naled or DDVP is transported into surface water, naled will degrade rapidly (half-life < 1 day) and DDVP will persist slightly longer (half-life ~ 5 days). Therefore, the impact of both of these chemicals on chronic surface water concentrations will be minimal and approach 0.0 ppb (p20).



## REFERENCES

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